

(19) Federal Republic  
of Germany

(12) Unexamined Patent  
Application  
(11) DE 197 32 313 A1

(51) Int. Cl. <sup>6</sup>:

C 08 G 18/32  
C 08 G 18/10  
C 08 L 75/04  
C 09 D 175/04  
B 05 D 5/00  
//C07C 211/55,E04B  
1/62

German Patent Office

(21) File no.: 197 32 313.8  
(22) Appl. date: 28. 7.97  
(43) Date laid 5. 2.98  
open for pub.  
insp.:

(30) Convention priority:  
8-202458 31.07.96 JP

(71) Applicant:  
I C K Co., Ltd., Tokio/Tokyo, JP

(74) Representative:  
Beetz und Kollegen, 80538 Munich

(72) Inventor:  
Oyaizu, Yoshijiro, Yaizu, Shizuoka, JP

(54) Polyurethane resin composition curable at room temperature

(54) A polyurethane resin composition curable at room temperature is proposed which is suitable for use as watertight coating material in construction. The composition is a mixture of a polyol terminated with isocyanate groups and a polyamine constituent as curing agent and advantageously has a moderately strong curing reaction, with the result that a reasonable processing time after the mixing of the constituents is ensured even at a hot time of year, wherein the processing time and the curability are well-balanced and the surface becomes rapidly free from stickiness even at a cold time of year. The characteristic feature of the inventive composition is the use of a specific polyamine curing agent, the main constituent of which is a 3,3',5,5'-tetraalkyl-4,4'-diaminodiphenylmethane in which each of the alkyl groups has 1 to 4 carbon atoms.

The invention relates to a novel polyurethane resin composition curable at room temperature or, in particular, a polyurethane resin composition curable at room temperature which can be cured so rapidly even at relatively low temperatures that it is free from surface stickiness within a short time and is  
5 nevertheless well-balanced at high temperatures in respect of the processing time and the curing behaviour. The inventive polyurethane resin composition has the advantage that it causes no problems due to foaming in the course of the curing reaction, with the result that a coating based on a cured polyurethane resin with high hardness and other excellent physical properties  
10 and with good final surface workability (finishing) results which can be used as a watertight coating material for processing on site.

As is known, watertight coating compositions and compositions for final surface working of floors based on polyurethane resin are used in very large  
15 quantities in construction for final surface working of the roofs of buildings, to make balconies and corridors watertight, to provide sports stadiums with elastic covers, etc. The compositions curable at room temperature, based on polyurethane resin, for use in the above-mentioned applications by processing on site are, as is most common in the state of the art, formulated with a  
20 prepolymer which is terminated by isocyanate groups at the chain ends of the molecule, namely as reaction product of a polyol compound, for example polypropylene ether glycols, and an aromatic diisocyanate compound, for example a tolylene diisocyanate, and a curing agent for the prepolymer which is typically 4,4-methylenebis(2-chloroaniline), which is called MOCA hereafter.  
25 The polyurethane compositions are normally delivered in two packs, one of which contains the prepolymer component and the other the curing agent, wherein the contents of the two packs are mixed together at the processing site immediately before use, with the result that the curing of the composition takes place quickly at room temperature.

30 The above-mentioned MOCA as curing agent for polyurethane prepolymers is a solid compound at room temperature with relatively high crystallinity and low miscibility with organic solvents, including plasticizers, which sometimes causes problems when handling. Nevertheless, MOCA is practically the only

compound which is suitable for use as curing agent for polyurethane resin compositions curable at room temperature, because it reacts only moderately strongly with the isocyanate ends of the prepolymer, with the result that a reasonable processing time results, by which is meant the time from the mixing of the prepolymer and curing agent to the moment at which the thoroughly mixed composition, in which the curing reaction proceeds with increasing viscosity even at room temperature, maintains a viscosity of for example 60,000 centipoise or less, which is suitable for problem-free coating work on site, and because the cured polyurethane resin layers have excellent properties which fulfil the requirements for watertight coating compositions based on polyurethane which are specified in JIS (Japanese Industry Standard) A 6021.

Although MOCA is usually used in the form of a solution, e.g. dissolved in a polyalkylene ether polyol as a constituent of the curable composition with relatively high solvent power for MOCA, it is essential, due to the different reactivity of MOCA with the prepolymer and with the polyol, that the polyurethane composition curable at room temperature is mixed with a heavy metal-containing catalyst such as for example an organotin compound in order to ensure a uniform process of these reactions at room temperature. A problem that sometimes occurs with such a coating composition is that, even with the addition of the above-mentioned catalyst, the progress of the curing reaction at a cold time of year is not rapid enough, with the result that the surface of the coating remains sticky for longer, although a curing seems to take place in the body of the coating, with the result that a serious delay is caused until the next processing step, for example the top finish coating, which can be carried out only on a non-sticky surface. Naturally, these problems associated with the delayed curing can be overcome by increasing the quantity of catalyst, whereby however a disadvantage is unavoidable, namely the reduction of the heat resistance of the cured coating. At a hot time of year, on the other hand, it is difficult with the mixture of the above-mentioned catalyst in the composition with the polyurethane resin curable at room temperature to obtain a good balance between the processing time and the curability of the composition, wherein the additional problem arises that a

foaming can occur in the coating as a result of the influence of moisture in the atmosphere when work is carried out in an environment with a high temperature and high moisture.

- 5    Moreover, MOCA is a toxic chemical substance, with the result that its use is subject to regulations under which exposure to MOCA must be avoided as far as possible in the workplace environment.

10    There was proposed some years ago a highly reactive polyurethane resin composition curable at room temperature which is prepared from a curing agent the main cross-linker of which in the form of an aromatic polyamine is a diethyltoluene diamine, and a prepolymer which contains an isocyanate compound based on a 4,4'-diphenylmethane diisocyanate, by mixing this without delay in a high-pressure impact mixing machine, which is followed by  
15    the extrusion of the thoroughly mixed composition into a mould in which the composition is cured to form a moulding. This process, which is called the RIM moulding process, is widely used to produce different types of car parts and similar. As a further development of the RIM process, the above-mentioned highly reactive polyurethane resin composition curable at room  
20    temperature is increasingly used for watertight coatings, wherein the thoroughly mixed composition is sprayed onto the surface of the support, with the result that a watertight polyurethane-based coating is formed by the immediate curing reaction.

- 25    A problem with the above-described highly reactive polyurethane composition is that its curing speed is so high that the composition gels within only approximately 10 s of mixing the curing agent and the prepolymer, which in the case of spray-coating results in a scattering of the mist and an unavoidable deterioration in the flow behaviour, while on the other hand the  
30    composition cannot be applied manually in practice, due to the too-short processing time.

As already described above, each of the conventional polyurethane resin compositions curable at room temperature has different disadvantages as a

watertight coating material and causes different problems. The development of a polyurethane resin composition curable at room temperature for watertight coatings which can be processed stably throughout the year and cured within a few hours, so that the top-finish coating is possible as the next  
5 step, which reduces the processing time and saves costs, is very desirable.

In view of the above-described problems and disadvantages of the state of the art, different proposals and tests have been carried out in recent years in respect of polyurethane resin compositions curable at room temperature  
10 which are based on a combination of a prepolymer, the main constituent of which is a polymer terminated by isocyanate groups as reaction product of a tolylene diisocyanate and a polyol compound, and a curing agent, the main constituent of which is an aromatic polyamine compound. For the above-mentioned curing agent, the unexamined Japanese patents 7-330854 and 7-  
15 330855 propose for example a mixture of a diethyltoluene diamine and a secondary aromatic amine compound, the unexamined Japanese patent 8-41156 proposes a mixture of a diethyltoluene diamine and methylbis(methylthio)benzene diamine, and the unexamined Japanese patent 8-34829 proposes a mixture of a diethyltoluene and MOCA.

20 Each of these mixtures, based on an aromatic polyamine, proposed as curing agent is essentially a mixture of diethyltoluene diamine as a first aromatic polyamine compound and a further aromatic polyamine compound. A problem with such a curing agent is that the hardness and the mechanical strength, for  
25 example the tensile strength and the tear strength, of the cured polyurethane resin composition decrease when the proportion in the mixture of the second aromatic polyamine compound is increased.

In view of the above-described problems and disadvantages of the  
30 conventional compositions, curable at room temperature, based on polyurethane resin of the state of the art, an object of the present invention is the provision of a novel composition, curable at room temperature, based on polyurethane resin, which is suitable for use as a watertight coating material which is curable within a short time at low temperatures, with the result that

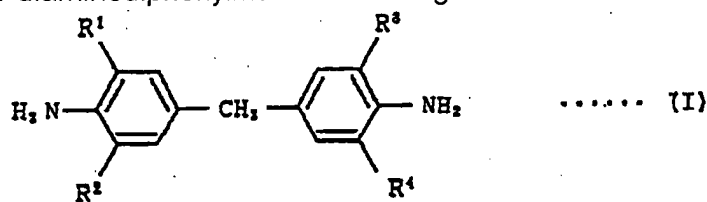
the surface rapidly becomes free of stickiness, and which is well-balanced in respect of the processing time and the curability at high temperatures, with the result that a coating with a good surface quality and a high hardness and excellent mechanical strength, e.g. tensile strength and tear strength, results without foaming.

To achieve the above-described object, the inventors carried out extensive studies and found that the object can be fully achieved if the composition, curable at room temperature, based on polyurethane resin has a prepolymer terminated by isocyanate groups and a specific curing agent, which is a tetraalkyldiaminodiphenylmethane with a specific molecule structure, optionally combined with a diethyltoluene diamine compound as second aromatic polyamine compound.

Thus the composition, curable at room temperature, based on polyurethane resin according to the present invention is a mixture which contains:

(A) a prepolymer terminated by isocyanate groups, which is a reaction product of a tolylene diisocyanate and a polyol compound, and

(B) a curing agent based on an aromatic polyamine, which is a 3,3',5,5'-tetraalkyl-4,4'-diaminodiphenylmethane of the general formula:



in which each of the groups  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is, independently of the others, an alkyl group with 1 to 4 carbon atoms, as first aromatic polyamine compound, optionally combined with a second aromatic polyamine compound, which is a diethyltoluene diamine in a quantity which does not exceed 90 wt.-% of the overall weight of the first and second aromatic polyamine compounds,

wherein the ratio of components (A) and (B) is such that the equivalent ratio of the isocyanate groups in component (A) to the amino groups in component (B) is in the range from 0.8 to 2.0.

- 5 It is preferred in particular that the prepolymer terminated by isocyanate groups as component (A) is a reaction product of a polypropylene ether polyol or polyethylene polypropylene ether polyol with a molecular weight in the range from 400 to 8000 and a tolylene diisocyanate compound. The tolylene diisocyanate compound is preferably 2,4-tolylene diisocyanate.

10

The composition, curable at room temperature, based on polyurethane resin according to the invention is illustrated in more detail below.

- Component (A) of the inventive composition is a urethane prepolymer, terminated by isocyanate groups, which is a reaction product of a tolylene diisocyanate compound and a polyol compound. The tolylene diisocyanate compound, as one of the reactants for the preparation of the prepolymer, is not subject to particular restrictions, and any isomer can be used, either alone or in the form of a combination of two isomer compounds, although 2,4-tolylene diisocyanate is preferred or the 2,4-isomer is to constitute at least 80% or even more preferably at least 85% of the isomer mixture, as isomers other than the 2,4-isomer may possibly result in a reduction in the processing time of the polyurethane resin composition. However, the use of a commercially available tolylene diisocyanate product whose 2,4-isomer content is sometimes less than 65% is not ruled out because of this situation.

- The polyol compound, as the other reactant for the preparation of the prepolymer, which forms component (A), is likewise not subject to particular restrictions and can be selected from polyether polyol compounds, polyester polyol compounds and polycaprolactone polyol compounds which are usually used for the preparation of a urethane prepolymer. However, it is preferred that the polyol compound is a polyalkylene ether polyol which is a liquid with a low viscosity at room temperature and has a molecular weight in the range from 400 to 8000.

In particular, the polyol reactant is preferably selected from polypropylene ether polyols and polyethylene polypropylene ether polyols and combinations of same.

5

The prepolymer terminated by isocyanate groups as component (A) furthermore preferably contains the isocyanate groups in a quantity in the range from 1.5 to 7.0 wt.-%. If the isocyanate groups content of the prepolymer is too low, the coating film comprising the cured polyurethane composition does not acquire a high mechanical strength, while in the case of too high an isocyanate groups content the processing time of the curable composition would be inappropriately shortened, as a result of which the use becomes inconvenient and moreover the problem arises that the cured coating has too high a hardness and only a slight expansion is possible.

15

Naturally, component (A) need not be a single urethane prepolymer, but can optionally be a combination of two or more types of prepolymers which were prepared in different formulations.

20 The other essential constituent, namely component (B), of the inventive polyurethane composition curable at room temperature is a curing agent, which is a 3,3',5,5'-tetraalkyl-4,4'-diaminodiphenylmethane which is represented by the general formula (I) given above, namely as first aromatic polyamine compound which is optionally combined with a second aromatic  
25 polyamine compound, which is a diethyltoluene diamine, provided that the first aromatic polyamine compound constitutes at least 10 wt.-%, relative to the overall weight of the first and the second polyamine compounds. If the proportion of the first aromatic polyamine compound in the combination of the first and second polyamine compounds is too small, the reactivity of the curing agent with the prepolymer which forms component (A) is not so moderately  
30 strong that a desired duration for the processing time of the curable composition results, wherein yet a further problem is connected with this, namely that the mechanical properties of the cured coating obtained with the



composition resemble those of the cured coating obtained only by using a diethyltoluene diamine as curing agent.

5 Particular examples of the 3,3',5,5'-tetraalkyl-4,4'-diaminodiphenylmethane represented by the general formula (I) given above, in which each of the groups  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are selected from methyl, ethyl, isopropyl and isobutyl groups, are:

3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane,  
10 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane,  
3,3'-dimethyl-5,5'-diethyl-4,4'-diaminodiphenylmethane,  
3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenylmethane,  
3,3'-dimethyl-5,5'-diisopropyl-4,4'-diaminodiphenylmethane,  
3,3'-dimethyl-5,5'-diisobutyl-4,4'-diaminodiphenylmethane,  
15 3,3'-diethyl-5,5'-diisopropyl-4,4'-diaminodiphenylmethane,  
3,3'-diethyl-5,5'-diisobutyl-4,4'-diaminodiphenylmethane and similar, although they are not subject to any particular restriction. These diamine compounds can be used either singly or in the form of a combination of two or more types, as required.

20

The diethyltoluene diamine compound, which is optionally used as a second aromatic polyamine compound in combination with the above-defined first aromatic polyamine compound as component (B), can be any or any combination of the isomeric compounds, for example 3,5-diethyltoluene-2,4-  
25 diamine, 3,5-diethyltoluene-2,6-diamine and similar. Each of these diamine compounds is liquid at room temperature. An isomer mixture of the diamine compounds is commercially available and can be used as such, for example the product sold by the Ethyl Corporation under the trade name Ethacure 100.

30 The above-mentioned first and second diamine compounds are well compatible with each other, as each is an aromatic diamine compound with similar alkyl groups as substituents at the aromatic core. They are furthermore easily miscible with plasticizers and polyol compounds.

The polyurethane resin composition curable at room temperature according to the invention is advantageous on account of the moderate curing speed of the composition formulated with the above-defined specific curing agent as component (B), as the curing speed of the composition is higher than the curing speed of the composition formulated with MOCA alone, but lower than that of the composition formulated with the diethyltoluene diamine alone, with the result that the inventive composition is less sensitive to the influence of moisture, which is unavoidably contained per se in the composition or comes from the environment at the processing site, whereby a cured coating with excellent surface quality results which is free from defects such as bubbles due to foaming and from residual surface stickiness.

The curable polyurethane composition of the invention can optionally be compounded with a plasticizer, which can be any customary plasticizer, for example dioctyl phthalate, dioctyl adipate, tricresyl phosphate, chlorinated paraffins and similar. The plasticizer, where it is used, is usually compounded beforehand with the curing agent as component (B) before it is mixed with component (A), but the prepolymer can also contain as component (A) part of the plasticizer. The quantity of plasticizer, where it is used, should not exceed 130 parts by weight per 100 parts by weight of the prepolymer as component (A). If the plasticizer quantity is too high, the coating of the cured polyurethane composition would be defective, due to the possible bleeding of the plasticizer at the surface of the cured layer or due to a reduction in its mechanical strength. As required, the inventive polyurethane resin composition can furthermore optionally be mixed with a catalytic compound, e.g. organotin compounds, in a quantity that does not exceed 3 wt.-%, relative to the prepolymer, with the result that the curing reaction of the composition according to the invention is moderately strongly accelerated.

An alternative method of achieving a plasticizer effect on the inventive polyurethane resin composition after curing is to mix the curing agent as component (B) with a polyol compound as plasticizers equivalent. The polyol compound used for this purpose is for example polypropylene ether polyols and polyethylene polypropylene ether polyols with a molecular weight in the

range from 400 to 8000. The quantity of polyol compound, if mixed with the curing agent, should not exceed 50 parts by weight per 100 parts by weight of the prepolymer as component (A). If the quantity is too high, the coating of the inventive composition would be defective after curing, due to the possible  
5 bleeding of the polyol compound at the surface or to a possible reduction in mechanical strength.

The curing agent as component (B) can furthermore be mixed as required with different types of known additives which are customarily used in curable  
10 polyurethane resin compositions, for example inorganic fillers such as calcium carbonate, talc, kaolin alumina, zeolite and diatomaceous earth, pigments such as chromium oxide, titanium dioxide, red iron oxide, yellow iron oxide and carbon black, stabilizers such as hindered amine compounds, hindered phenol compounds and benzothiazole compounds, defoaming agents,  
15 inhibitors of dyestuff decomposition, dispersion aids, sedimentation inhibitors and thickening agents.

The commercial delivery form of the inventive polyurethane resin composition curable at room temperature consists of two packs, one of which is for the  
20 prepolymer terminated by isocyanate groups as component (A) and the other for the curing agent as component (B) in combination with the above-described other optional constituents. The contents of the two packs are mixed together, with the result that a uniform composition results at the processing site immediately prior to application as coating to the support  
25 surface, whereby the curing reaction of the composition is initiated and progresses, obtaining a cured coating of the composition until it is watertight. The mixing ratio of the two components is preferably such that the equivalent ratio of isocyanate groups in the prepolymer and the amino groups in the curing agent is in the range from 0.8 to 2.0. If the quantity of prepolymer is too  
30 small, a substantial quantity of the polyamine compound is not reacted, whereby bleeding occurs at the surface, which possibly results in a discoloration of the coating. On the other hand, if the quantity of prepolymer is too large, the curing speed of the composition, and the mechanical strength of the cured coating, drop.

The above-described polyurethane resin composition curable at room temperature according to the invention can be used very satisfactorily as a watertight coating material and as a finish-coating material for floor coverings; because the composition and also the cured coating comprising the composition have many excellent properties. As the inventive curable composition displays a moderately strong curing behaviour, the mixing processes and the coating operations can be carried out by hand with the inventive composition, although the mixing and the coating can also be mechanized using a suitable automatic mixing machine, for example static mixers and dynamic mixers.

The polyurethane resin composition curable at room temperature according to the invention is explained in more detail below by examples, without however limiting the scope of the invention in any way. The examples are preceded by a characterization of the prepolymer constituents and curing agents and also the other optional constituents which are used in the examples. In the following description, the quoted parts are always "parts by weight".

#### Prepolymer constituents

PPG-2000: polypropylene etherdiol with an average molecular weight of 2,000 and a hydroxyl number of 56.0 mg KOH/g, a product of Dai-ichi Kogyo Seiyaku Co., Ltd.

T-4000: polypropylene ethertriol with an average molecular weight of 4,000 and a hydroxyl number of 42.1 mg KOH/g, a product of Dai-ichi Kogyo Seiyaku Co., Ltd.

TDI-80: a mixture in the ratio by weight 8:2 of 2,4- and 2,6-tolylene diisocyanates with an isocyanate content of 48.3 wt.-%, a product of Nippon Urethane Kogyo Co., Ltd.

TDI-100: 2,4-tolylene diisocyanate with an isocyanate content of 48.3 wt.-%, a product of Nippon Urethane Kogyo Co., Ltd.

#### Curing agents

5

DETDA: diethyltoluene diamine with an amine number of 629 mg/KOH/g, Ethacure 100, a product of the Ethyl Corporation.

10 TEDDM: 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane with an amine number of 306.0 mg KOH/g, Kayabond C-300, a product of Nippon Kayaku Co., Ltd.

15 TPDDM: 3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenylmethane with an amine number of 304.9 mg KOH/g, Kayabond C-400, a product of Nippon Kayaku Co., Ltd.

MEDDM: 3,3'-dimethyl-5,5'-diethyl-4,4'-diaminodiphenylmethane with an amine number of 395.5 mg KOH/g, Curehard MED, a product of Ihara Chemical Industry Co., Ltd.

20

MOCA: 3,3'-dichloro-4,4'-diaminodiphenylmethane with an amine number of 420.2 mg KOH/g, Cuamine MT, a product of Ihara Chemical Industry Co., Ltd.

#### Others

25

D-5000: polypropylene etherdiol with a molecular weight of 5,000 and a hydroxyl number of 22.4 mg/KOH/g, a product of Dai-ichi Kogyo Seiyaku Co., Ltd.

30 DOP: dioctylphthalate, a product of Dai-nippon Ink Chemical Co., Ltd.

NS-100: calcium carbonate filler, a product of Nitto Funka Shoji Co., Ltd.

P-420: defoaming agent, a product of Kusumoto Kasei Co., Ltd.

### Example 1

5 A urethane prepolymer was prepared according to a process in which 86.2 parts PPG-200 and 13.8 parts TDI-100 were placed in a flask with a removable 4-necked closure and the mixture circulated and gradually heated to a temperature of 80°C under a stream of nitrogen gas, followed by further 7 h circulation at the same temperature, in order to bring about the reaction of the reactants, followed by cooling to room temperature.

10

The analysis carried out according to a method specified in JIS K 1588 of the thus-prepared prepolymer showed 3.03 wt.-% isocyanate groups and an equivalent ratio of isocyanate groups to hydroxyl groups of 1.84.

15

Separately, a curing agent for the prepolymer was prepared as follows. 3.5 parts TEDDM and 72.5 parts DOP were heated in a polypropylene beaker, with the result that a uniform mixture formed which was mixed with 3.5 parts DETDA and 1.0 parts P-420 and then mixed manually with a spatula with 119.5 parts NS-100, followed by kneading in a three-roll mill.

20

A polyurethane resin composition curable at room temperature was prepared by uniformly mixing the above-prepared prepolymer and the curing agent in a ratio by weight of 1:2 for 2 min in a polypropylene beaker with a dispersion mixing machine, with the result that an equivalent ratio (isocyanate groups):(amino groups) of 1.17 resulted, whereupon the composition underwent assessment tests, for example in respect of:

25

(1) the processing time in minutes, which was the time from the mixing of the prepolymer and the curing agent up to the moment at which the viscosity of the composition rose to 60,000 centipoise,

30

(2) the time until the surface was free from stickiness in hours, this being the time which the surface exposed to air of the composition required to be free from stickiness when touched with a finger, and

(3) mechanical properties of a layer of the composition with a thickness of 1.5 to 2.0 mm which was cured on an aluminium sheet coated with Teflon by standing for 7 days at 20°C, wherein the measurements were taken according to the methods specified in JIS K 6021.

The results obtained in the assessment tests are summarized in Table 1 below.

#### Example 2

The experimental method was essentially the same as in Example 1, with the difference that the curing agent was prepared from 3.7 parts DETDA, 3.7 parts TPDDM, 72.1 parts DOP, 119.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:2 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.17.

The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

#### Example 3

The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 3.3 parts DETDA, 3.3 parts MEDDM, 72.9 parts DOP, 119.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:2 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

#### Comparison example 1

5 The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 5.4 parts DETDA, 74.1 parts DOP, 119.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:2 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

10

#### Comparison example 2

15 The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 8.1 parts MOCA, 71.4 parts DOP, 119.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:2 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

20 The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

#### Comparison example 3

25 The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 3.3 parts DETDA, 3.3 parts MOCA, 119.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:2 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

30 The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

#### Example 4



The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 5.1 parts DETDA, 0.6 parts MEDDM, 27.8 parts DOP, 65.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:1 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

10

#### Example 5

The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 4.5 parts DETDA, 1.5 parts MEDDM, 27.8 parts DOP, 65.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:1 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

20 The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

#### Example 6

25 The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 3.3 parts DETDA, 3.3 parts MEDDM, 27.4 parts DOP, 65.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:1 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

30

The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

### Example 7

The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 1.9 parts DETDA, 5.6  
5 parts MEDDM, 27.5 parts DOP, 64.0 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:1 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

10 The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

### Example 8

15 The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 8.6 parts MEDDM, 26.4 parts DOP, 64.0 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:1 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

20 The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

### Comparison example 4

25 The experimental method was substantially the same as in Example 1, with the difference that the curing agent was prepared from 5.4 parts DETDA, 28.6 parts DOP, 65.0 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:1 relative to the weight, with the result that  
30 the equivalent ratio (isocyanate groups):(amino groups) was 1.18.

The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

### Example 9

The experimental method was substantially the same as in Example 1, with the difference that the prepolymer, which contained 3.3 wt.-% isocyanate groups with an equivalent ratio of isocyanate groups to hydroxyl groups of 2.0, was prepared from 34.6 parts T-4000, 51.8 parts PPG-2000 and 13.6 parts TDI-80 and the curing agent from 3.7 parts DETDA, 3.7 parts TEDDM, 72.1 parts DOP, 119.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:2 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.20.

The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

15

### Example 10

The experimental method was substantially the same as in Example 9, with the difference that the curing agent was prepared from 3.6 parts DETDA, 3.6 parts MEDDM, 72.3 parts DOP, 119.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:2 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.19.

The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

25

### Example 11

The experimental method was substantially the same as in Example 9, with the difference that the curing agent was prepared from 2.7 parts DETDA, 2.7 parts MEDDM, 32.3 parts DOP, 40.0 parts DD-5000, 119.5 parts NS-100 and 1.0 parts P-420. The mixing ratio of prepolymer to curing agent was 1:2 relative to the weight, with the result that the equivalent ratio (isocyanate groups):(amino groups) was 1.20.

30

The results of the assessment tests, which were carried out as in Example 1, are given in Table 1.

5

Table 1

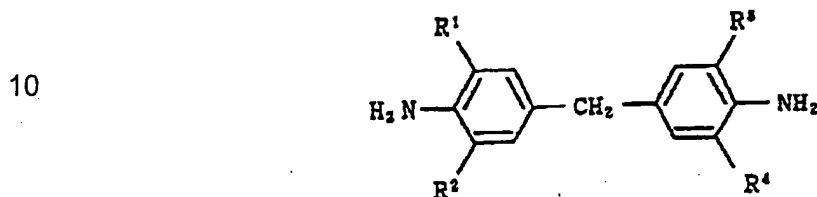
	Processing time	Time until surface is free from stickiness	Shore A hardness	Tensile strength kg/cm <sup>2</sup>	Expansion %	Tear strength kg/cm
	min	h				
Ex. 1	70	5	62	42	733	22
Ex. 2	70	5	63	45	728	21
Ex. 3	65	4	62	44	805	23
Ex. 4	26	3	69	76	735	33
Ex. 5	28	3	71	81	750	32
Ex. 6	28	3	73	84	708	35
Ex. 7	30	3	72	83	658	38
Ex. 8	30	3	79	95	665	46
Ex. 9	39	3	63	45	683	24
Ex. 10	34	3	64	48	752	27
Ex. 11	38	5	60	42	850	22
Comp.-Ex. 1	50	5	55	39	850	19
Comp.-Ex. 2	200	24	45	32	860	15
Comp.-Ex. 3	85	8	50	36	810	16
Comp.-Ex. 4	23	3	64	63	693	29

## Claims

1. Polyurethane resin composition, curable at room temperature, which is a mixture which contains:

5 (A) a prepolymer terminated by isocyanate groups, which is a reaction product of a tolylene diisocyanate and a polyol compound, and

(B) a curing agent based on an aromatic polyamine, which is a 3,3',5,5'-tetraalkyl-4,4'-diaminodiphenylmethane of the general formula:



in which each of the groups R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is, independently of the others, an alkyl group with 1 to 4 carbon atoms, as first aromatic polyamine compound,

15 compound, optionally combined with a second aromatic polyamine compound, which is a diethyltoluene diamine in a quantity which does not exceed 90 wt.-% of the overall weight of the first and second aromatic polyamine compounds,

wherein the ratio of components (A) and (B) is such that the equivalent ratio of the isocyanate groups in component (A) to the amino groups in component (B) is in the range from 0.8 to 2.0.

2. Polyurethane resin composition, curable at room temperature, according to claim 1, wherein the prepolymer terminated by isocyanate groups as component (A) is a reaction product of the reaction of a polypropylene ether polyol or polyethylene polypropylene ether polyol with a molecular weight in the range from 400 to 8000 with a tolylene diisocyanate compound.

3. Polyurethane resin composition, curable at room temperature, according to claim 1, wherein the tolylene diisocyanate compound is 2,4-tolylene diisocyanate.

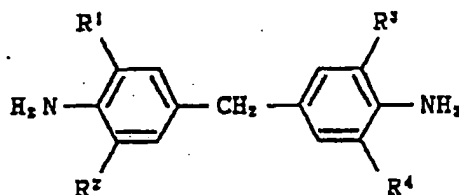
4. Polyurethane resin composition, curable at room temperature, according to claim 1, wherein the prepolymer terminated by isocyanate groups as component (A) contains 1.5 wt.-% to 7.0 wt.-% of the isocyanate groups.

5. Polyurethane resin composition, curable at room temperature, according to claim 1, wherein the alkyl groups with 1 to 4 carbon atoms are selected from methyl, ethyl, isopropyl and isobutyl groups.

6. Use of a polyurethane resin composition, curable at room temperature, which is a mixture which contains:

(A) a prepolymer terminated by isocyanate groups, which is a reaction product of a tolylene diisocyanate and a polyol compound, and

(B) a curing agent based on an aromatic polyamine, which is a 3,3',5,5'-tetraalkyl-4,4'-diaminodiphenylmethane of the general formula:



in which each of the groups R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is, independently of the others, an alkyl group with 1 to 4 carbon atoms, as first aromatic polyamine compound, optionally combined with a second aromatic polyamine compound, which is a diethyltoluene diamine in a quantity which does not exceed 90 wt.-% of the overall weight of the first and second aromatic polyamine compound, wherein the ratio of components (A) and (B) is such that the equivalent ratio of the isocyanate groups in component (A) to the amino groups in component (B) is in the range from 0.8 to 2.0, as watertight coating material.